

REMARKS/ARGUMENTS

This Reply is in response to the Office Action dated January 11, 2006 and is accompanied by a petition for a one-month extension of time along with an authorization to charge the required statutory fee for the extension.

In this Reply, claims 1-4, 26 and 32 have been amended and claims 31 and 36 have been cancelled. Claims 72-74 have been added. Support for the recited pH of 1 recited in claim 72 can be found in Example 6 which recites a pH range of 1 to 13, while support for a pH of 6 can be found in the summary as well as in original claim 33. New independent claim 73 recites "A slurry for chemical mechanical polishing (CMP), comprising: a bulk solution, said bulk solution being in a pH range of 1 to 6 or 8 to 13, and a plurality of nanoporous comprising particles". Support for the recited pH ranges can be found in Applicants' summary. No new matter has been added.

In Applicants' Reply filed on October 27, 2005, claim 1 was amended to recite a slurry comprising "a plurality of *nanoporous* comprising particles" to distinguish U.S. 6,048,577 to Garg who discloses a polishing slurry including only nanosize (but not nanoporous) particles. However, in the instant action, although the anticipation rejections based on Garg and obviousness rejections based on Garg in view of U.S. 6,458,017 to Li were withdrawn, the Examiner identified a new reference to formulate new obviousness rejections.

Specifically, claims are rejected based on newly cited U.S. Pat. 5,055,019 to Meyer et al. (cited for nanoporous particles) combined with Garg. According to the Examiner:

Garg teaches nano-sized powder of alpha alumina having silica coating thereon (column 5, lines 7-10). Garg further teaches a polishing slurry is comprised of a alumina powder has a silica coating wherein 95% of the particles have widths of from 20 to about 50 nanometers while less than 5% have particle sizes greater than 100 nanometers and is dispersed in a liquid dispersion medium (claims 6 and 9). The aforementioned reads on,

A slurry for chemical mechanical polishing (CMP), comprising:
a bulk solution; and

a plurality of particles, in claim 1; and
encompasses an average particle size of said nanosize comprising particles is less than 500 nm, in claim 9 and is from 200 to 500 nm, in claim 10.

Garg differs if failing to teach a plurality of nanoporous comprising particles, in claims 1, 5, 6, and 9.

Meyer discloses boehmitic alumina compounds having Al_2O_3 and the compounds have a pore radii in the range of 3 to 100 nm (Abstract and column 1, lines 6-10), which reads on a plurality of nanoporous comprising particles.

Since Meyer illustrates a plurality of nanoporous comprises particles is known, then it would have been obvious to one having ordinary skill in the art at the time the invention was made to modify Garg's slurry by employing compounds having a pore radii in the nm range as taught by Meyer, including applicants' specifically claimed range because such compounds can be used in polishing agents (Meyer, column 1, lines 11-16).

Applicants respectfully disagree with the assertion of obviousness based on Garg in view of Meyer. However, before reviewing the cited art, Applicants will review the claimed invention as now recited in amended claim 1 (copied below).

1. (Currently amended) A slurry for chemical mechanical polishing (CMP), comprising:
a bulk solution including at least one additive selected from the group consisting of
an oxidizer, a selective adsorption additive and a salt, and;
a plurality of nanoporous comprising particles.

The amendment to claim 1 thus adds an "additive selected from the group consisting of an oxidizer, a selective adsorption additive and a salt". Such additives are specific to chemical mechanical polishing (CMP), which is the basis of Applicants' claimed invention. Unlike CMP which relies on mechanical action as well as chemical action, general mechanical polishing, even when slurries are used, rely entirely on mechanical abrasion and thus do not include any of the recited additives recited in amended claim 1. For example, the oxidizer recited in claim 1 is clearly specific for the CMP of metals.

Applicants have included text which distinguishes CMP processing from both mechanical polishing (disclosed by Garg and Meyer) and chemical etching. This article was published in MRS Bulletin October 2002 (full copy attached; salient details copied below):

The CMP process is often confused with chemical etching, and/or mechanical polishing process. All the three processes achieve controlled material removal; however the mechanisms by which material removal is achieved are completely different. In a chemical etching process, material removal is achieved by a chemical reaction at the surface, resulting in the formation of dissolved species and subsequent transportation of the dissolved species from the surface. The etching rate/removal rate is constant and does not change with time. This is shown schematically in Fig. 3. In the CMP process, the chemical reactions between the chemicals and the metallic layers result in a thin, non-dissolving and chemically passivating surface film which is subsequently removed by the mechanical action of the particles. Initially the chemical reaction rate is high, but due to passivation effects, the reaction rate drops immediately. When the surface layer is removed by abrasive particles in the slurry, the surface film formation and passivation

phenomenon repeats itself (Fig. 3). Thus, static etch rate in a CMP process is quite low. In dielectric CMP, although surface passivation is not a critical issue, the formation of a soft hydrated gel-like layer on the surface is important to achieve high performance polishing.

In mechanical polishing, the removal of material takes place by direct interaction of particles on the original surface. The material removal in this case can be considered to be due to the classical abrasion wear mechanism which involves indentation and the removal of material by a scratching process. This material removal mechanism typically requires high energy because bonds have to be broken by mechanical forces only. Due to large energy requirements, the removal rates are typically much lower than CMP unless larger sized particles are used, in which case high surface defectivity is obtained. Thus, an inverse relationship typically exists between the rate of removal and the surface finish. In contrast, in a CMP process, the chemical modified surface layer is much easily removed because of its inherent nature: soft, ductile layer in the case of silica and more brittle layers in the case of metals such as tungsten, copper, etc. Figure 5 shows schematically the relationship between removal rate and surface finish for all three material removal processes.

Garg is entitled "Nano-sized alpha alumina particles having a silica coating thereon" and discloses nano-sized powders of alpha alumina can be obtained from a boehmite gel doped with a barrier-forming material such as silica that is then dried, fired and comminuted to powder form. The only mention of porosity in Garg regarding porosity is in the background regarding "porous nature of the boehmite particles" as copied below:

One of the problems in working with a boehmite gel to produce formed ceramic articles is that the gel cannot exceed about 65 wt % solids because of the *porous* nature of the boehmite particles. Thus there is a lot of water that needs to be driven off in the course of the drying process. In addition not only is there further shrinkage as a result of the elimination of the water associated with the boehmite, (which is of course alpha alumina monohydrate), but the phase change from the intermediate gamma phase (to which the boehmite first converts) to the final alpha phase also involves a shrinkage. Thus the direct fabrication of a ceramic product from boehmite is only practical for thin objects where the water loss can be relatively easily be accommodated and the shrinkages can be controlled.

In one embodiment, Garg's does disclose a polishing slurry comprising a powder dispersed in a liquid dispersion medium (claims 9 and 10). However, Garg does not mention CMP and does not disclose or suggest Applicants' claimed CMP slurry including the claimed "nanoporous comprising particles" or the newly recited "additive selected from the group consisting of an oxidizer, a selective adsorption additive and a salt".

Meyer is entitled "Process for the production of boehmitic aluminas" and discloses a process for the preparation of boehmitic alumina compounds having a purity of, at least, 99.95% Al_2O_3 . The compounds produced according to the invention have a pore radii in the range of 3 to 100 nm. The preparation of such compounds is carried out by, first, obtaining an alumina suspension from a neutral aluminum alkoxide hydrolysis and, then, aging the alumina suspension in an autoclave, preferably, at a steam pressure of 1 to 30 bar, corresponding to a temperature of 100 degree C. to 235 degree C., for between 0.5 and 20 hours. The aging step of the invention is preferably carried out with stirring at a peripheral speed of 1 to 6 m/s.

As noted above, to base an obviousness rejection of former claim 1 the Examiner combined Garg and Meyer based on the following reasoning:

Since Meyer illustrates a plurality of nanoporous comprises particles is known, then it would have been obvious to one having ordinary skill in the art at the time the invention was made to modify Garg's slurry by employing compounds having a pore radii in the nm range as taught by Meyer, including applicants' specifically claimed range because such compounds can be used in polishing agents (Meyer, column 1, lines 11-16).

Applicants acknowledge that Meyer mentions in a single place (cited by the Examiner) that the nanoporous particles according to Meyer can be used for "polishing". Applicants have copied the full paragraph below relied on by the Examiner.

In the neutral hydrolysis of aluminum alkoxides, e.g., as described in DE-AS 1 258 854, aluminas with a boehmite structure or α -alumina-aluminum oxide monohydrate are obtained. The products obtained have a maximum pore radius of 2 to 4 nm and can be used as pigments, fillers, polishing agents and catalyst carriers. *However, it is particularly desirable, in the case of carrier materials for catalysts and for separating gaseous components, that such aluminas are obtained with a pore volume or with pore radii in a specific range. It is particularly desirable to increase*

the pore volume of such aluminas and also to increase the pore radius, while maintaining a very narrow pore radius distribution.

Significantly, Meyer discloses the invention is "particularly desirable, in the case of carrier materials for catalysts and for separating gaseous components". Applicants note that in the case of catalysis, more surface area is clearly desirable as it increases surface area for the reaction to take place. In contrast, there is no apparent advantage in using porous particles for polishing (as compared to conventional solid particles). Significantly, particle porosity is well known by those having ordinary skill in the art to reduce the mechanical integrity of the particles. For example, one having ordinary skill in the art of mechanical polishing porosity would readily appreciate that porosity of any kind would mechanically weaken the particles and make the particles susceptible to fracture or even pulverization during mechanical polishing. Thus, since mechanical integrity is a known problem regarding porous particles and no advantages regarding porous particles are disclosed or known to those having ordinary skill in the art, porous particles including nanoporous particles are taught away from for mechanical polishing applications.

Moreover, Applicants can find no suggestion or motivation to modify Garg to add the nanoporosity disclosed in Meyer in any of the references of record in this case. MPEP 2143.01 entitled "Suggestion or Motivation to Modify the References" describes the required elements necessary under the Patent Law to properly support a finding of a motivation to modify references. A portion thereof is copied below:

In determining the propriety of the Patent Office case for obviousness in the first instance, it is necessary to ascertain whether or not the reference teachings would appear to be sufficient for one of ordinary skill in the relevant art having the reference before him to make the proposed substitution, combination, or other modification." In re Linter, 458 F.2d 1013, 1016, 173 USPQ 560, 562 (CCPA 1972).

Obviousness can only be established by combining or modifying the teachings of the prior art to produce the claimed invention where there is some teaching, suggestion, or motivation to do so found either explicitly or implicitly in the references themselves or in the knowledge generally available to one of ordinary skill in the art. "The test for an implicit showing is what the combined teachings, knowledge of one of ordinary skill in the art, and the nature of the problem to be solved as a whole would have suggested to those of ordinary skill in the art." In re Kotzab, 217 F.3d 1365, 1370, 55 USPQ2d 1313, 1317 (Fed. Cir. 2000). See also In re Fine, 837 F.2d 1071, 5 USPQ2d 1596 (Fed. Cir. 1988); In re Jones, 958 F.2d 347, 21 USPQ2d 1941 (Fed. Cir. 1992).

Regarding Applicants' recited nanoporosity, the Examiner asserts that the motivation to add the nanoporosity disclosed in Meyer to Garg's slurry is "because such compounds can be used in polishing agents".

Applicants respectfully traverse the above-provided motivation to add the recited nanoporosity to Garg's slurry particles. The single mention in Meyer that nanoporous particles can be used in polishing, without the recognition of any advantages thereof, does not provide the required "teaching, suggestion, or motivation" to modify be "found either explicitly or implicitly in the references themselves or in the knowledge generally available to one of ordinary skill in the art. Without the benefit of Applicants' application one having ordinary skill in the art would not specifically recognize the advantages of the recited nanoporosity for CMP described in Applicants' application which have unexpectedly found to provide improved CMP results. As noted above, nanoporosity is taught away since one having ordinary skill in the art of mechanical polishing would recognize that porosity of any kind would mechanically weaken the particles and make them susceptible to fracture or even pulverization. Accordingly, absent impermissible hindsight regarding Applicants' findings, one having ordinary skill in the art would not recognize a single advantage of nanoporosity for CMP particles as described by Applicants. Accordingly, since there is no motivation for one having ordinary skill in the art to modify Garg's slurry particles to add nanoporosity, and the mechanically compromised porous particles would

themselves teach away from use for polishing, amended claim 1 is believed to recite an inventive step and thus render claim 1 and claims dependent thereon patentable over the cited art.

In addition, following Applicants' amendment to claim 1, Applicants note that Garg and Meyer are now both clearly unrelated art relative to Applicants' claimed CMP slurry which now recites a CMP specific additive. Although Garg discloses a polishing slurry, the slurry is a simple mechanical polishing slurry. Meyer's single mention of the nanoporous particles for "polishing" does not mention a polishing slurry, nor clearly CMP. Accordingly, both Garg and Meyer are wholly unrelated to CMP. As noted above, while general mechanical polishing, even when slurries are used, rely entirely on mechanical abrasion, CMP relies on mechanical action as well as chemical action, and thus requires chemically active additive(s) to achieve the desired action. Applicants have copied MPEP 2141.01(a) below to emphasize that *at least Meyer is nonanalogous art.*

2141.01(a) Analogous and Nonanalogous Art

TO RELY ON A REFERENCE UNDER 35 U.S.C. 103, IT MUST BE ANALOGOUS PRIOR ART

The Examiner must determine what is "analogous prior art" for the purpose of analyzing the obviousness of the subject matter at issue. "In order to rely on a reference as a basis for rejection of an applicant's invention, the reference must either be in the field of applicant's endeavor or, if not, then be reasonably pertinent to the particular problem with which the inventor was concerned." In re Oetiker, 977 F.2d 1443, 1446, 24 USPQ2d 1443, 1445 (Fed. Cir. 1992). See also In re Deminski, 796 F.2d 436, 230 USPQ 313 (Fed. Cir. 1986); In re Clay, 966 F.2d 656, 659, 23 USPQ2d 1058, 1060-61 (Fed. Cir. 1992) ("A reference is reasonably pertinent if, even though it may be in a different field from that of the inventor's endeavor, it is one which, because of the matter with which it deals, logically would have commanded itself to an inventor's attention in considering his problem."); and Wang Laboratories Inc. v. Toshiba Corp., 993 F.2d 858, 26 USPQ2d 1767 (Fed. Cir. 1993).

Applying the above rule, Meyer is clearly outside Garg's field of endeavor, that being polishing slurries. Meyer is also not reasonably pertinent to the problem at hand, mechanically

polishing a surface using a slurry, as Meyer does not relate to slurries for polishing at all. Accordingly, Applicants submit that one having ordinary skill in the art reading Garg would not consider Meyer's nanoporous particles since Meyer is nonanalogous art to slurry-base polishing.

Some claims are believed to provide separate bases for patentability. For example, amended claim 2 recites "The slurry of claim 1, wherein said additive comprises said selective adsorption additive", such as a surfactant or surface active polymer. As taught in the present application, the claimed nanoporous slurry particles provide unexpected and highly advantageous results, particularly when used in conjunction with Applicants' selective adsorption additive comprising slurry recited in claim 2. Specifically, in this arrangement, because of the porous particle surface, the adsorption of surfactants or polymer additives can occur at different, and generally lower, concentrations as compared to bulk particles.

Moreover, claim 6 which recites "wherein said nanosize nanoporous particles comprise nanoporous cores coated with a solid material coating or first core material coated with a second material, said second material being a nanoporous coating" appears to have been improperly rejected because no basis in the cited art for the limitation recited is provided.

New independent claim 73 recites "A slurry for chemical mechanical polishing (CMP), comprising: a bulk solution, said bulk solution being in a pH range of 1 to 6 or 8 to 13, and a plurality of nanoporous comprising particles". The pH, like Applicants slurry additives recited in amended claim 1 are specific to CMP. In contrast, mechanical polishing slurries are essentially neutral (pH of 7). Accordingly, for reasons analogous to those described above relative to amended claim 1, claim 73 and its dependent claim are believed to recite an inventive step and thus be patentable over the cited art.

Conclusion

Accordingly, in view of the above, Applicants submit amended claim 1 which recites a slurry for chemical mechanical polishing (CMP), comprising a plurality of nanoporous comprising particles together with a bulk solution including at least one (CMP SPECIFIC) "additive selected from the group consisting of an oxidizer, a selective adsorption additive and a salt" is patentable over the cited art, as are claims dependent thereon. Similarly, new claim 73 which recites a slurry for chemical mechanical polishing (CMP), comprising a plurality of nanoporous comprising particles together with a bulk solution being in a (CMP SPECIFIC) pH range of 1 to 6 or 8 to 13 is patentable over the cited art, as is its dependent claim. Applicants have made every effort to present claims which distinguish over the cited art, and it is believed that all claims are now in condition for allowance. However, Applicants request that the Examiner call the undersigned if anything further is required by the Examiner prior to issuance of a Notice of Allowance for all claims.

Respectfully submitted,

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Advances in Chemical-Mechanical Planarization

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Abstract

The primary aim of this issue of *MRS Bulletin* is to present an overview of the current issues in chemical-mechanical planarization (CMP), also known as chemical-mechanical polishing, a process that is used in the semiconductor industry to planarize and smooth silicon wafers prior to a chip. The CMP process has been the fastest-growing semiconductor operation in the last decade, and the future opportunities include the introduction of copper-plated interconnects to address the topography issues associated with copper wiring. This issue begins by providing a fundamental understanding of the CMP process to the general practitioners in the field. Topics covered in this section include an overview of CMP, fundamental principles of slurry design, understanding of the slurry-polymer interactions, process integration issues, the formation of surface-free layers for copper polishing, understanding surface topography issues in shallow trench isolation, and emerging applications.

Keywords: chemical-mechanical planarization; chemical-mechanical polishing; CMP; copper interconnects; low-dielectric; nanotechnology; shallow trench isolation; slurry; polishing; slurry design.

Introduction

In the past decade, chemical-mechanical planarization (CMP), also known as chemical-mechanical polishing, has emerged as the fastest-growing operation in the semiconductor manufacturing industry, and it is expected to show equally explosive growth in the future.¹ It is estimated that more than 150 million planarization operations will be conducted this year, and that number is expected to double within the next three years.² This rapid increase will be fueled by the introduction of copper-based interconnects for logic and other devices.³ Other novel applications of CMP for next-generation nanoscale devices are rapidly emerging.

The market size for CMP equipment and consumables (slurries, pads, etc.) grew from \$250 million in 1996 to over \$1 billion in 2000.⁴ The consumables market, especially in the area of slurries, is quite robust and is expected to increase from the

present level of \$250 million to more than \$800 million within the next five years.⁵ The slurries, which typically contain particle-based abrasives and chemical additives, represent the largest value-added application of nanoparticles—a key area of nanotechnology that is currently garnering substantial funding from governmental organizations and private corporations. It has been estimated that CMP nanoparticles alone will constitute nearly 60% of the total \$1 billion worldwide market for nanopowders by 2005.

One of the unique aspects of CMP is that the process was invented, developed, and put into application by the industry itself without any significant interaction with academic institutions. Consequently, the whole process is shrouded in secrecy, with most of the literature available in the form of patents. The composition of the slurry is the most secretive element. A casu-

ality of this approach has been the lack of a fundamental understanding of the CMP process. This lack is further compounded by the large number of input variables (>20) and output variables (>4) that need to be optimized.⁶ Furthermore, the science of CMP is quite different from traditional semiconductor manufacturing technology, which is based on film deposition, ion implantation, photolithography, thermal annealing, vapor-phase processing, and so on.⁶ For CMP, an entirely new knowledge base and set of skills, involving particle technology, corrosion, tribology and tribochemical phenomena, wet and surface chemistry, fluid flow, and mechanical properties of polymers, are considered essential.⁷ These areas traditionally have not been the focus of semiconductor manufacturing practitioners.

All of these factors have contributed to the impression that CMP is more of an art than a science. Furthermore, misconceptions exist among semiconductor manufacturing practitioners because of a failure to distinguish CMP from other controlled material-removal techniques such as chemical etching and mechanical polishing. As an example, the most widely used fundamental equation in CMP, Preston's law, is nonetheless flawed, as it is solely based on concepts derived from mechanical polishing.^{8,9} Further insights into this aspect are discussed in the next section.

The articles in this issue not only provide glimpses into technological advances in the CMP process, but also give a solid framework for understanding CMP phenomena. Important materials-related issues are highlighted. This overview provides a brief description of the process, some key advancements, and emerging applications of CMP.

Brief Description of the Process

CMP combines chemical and mechanical interactions to planarize metal and dielectric surfaces using a slurry composed of chemicals and submicron-sized particles.¹ A schematic diagram of the CMP operation is shown in Figure 1. The slurry is fed onto a polishing pad made of a porous polymer. By moving the pad across the wafer in a circular, elliptical, or linear motion, the wafer surface is polished. The polymeric pad performs several functions, including uniform slurry transport, distribution, and removal of the reacted products, and uniform distribution of applied pressure across the wafer. In a typical CMP process, the chemicals interact with the material to form a chemically modified surface. Simultaneously, the abrasives in the slurry mechanically interact with the chemically modified surface layers, resulting in material removal.¹⁰

Advances in Chemical-Mechanical Planarization

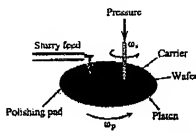


Figure 1 Schematic diagram of a typical chemical-mechanical planarization (CMP) process. ω_c and ω_p refer to the angular velocity of the carrier and the platen, respectively.

A mechanistic understanding of the CMP process can be developed by studying the wafer-pad-slurry interactions that occur at both the micro- and nanoscale (Figure 2).^{12,14} At the microscale, the rough pad carrying the particle-based slurry interacts with the surface of the wafer. It is generally believed that the particles, which are between the wafer and the pad, participate in a mechanical abrasion process that results in material removal. At the nanoscale, the kinetics of the formation and removal of the thin surface layer controls CMP output parameters such as removal rate, surface planarity, surface defectivity, and slurry selectivity (the polishing rate of the top layer as compared with the underlying layer).

Although the CMP process is intuitively quite simple, achieving a more detailed understanding has been limited primarily by the large number of input variables in the polishing process. Table 1 lists the various systems-level variables in CMP. They include slurry variables (such as particles and chemicals), pad variables, tool variables (down pressure and linear velocity), and substrate variables (pattern density, etc.).¹⁵ The total number of variables can exceed 20, making the process difficult to understand and control. Time-dependent contributions by some of these variables cause further complexities in the process.

As mentioned earlier, the CMP process is often confused with chemical etching or mechanical polishing. All three processes achieve controlled material removal; however, the mechanisms by which material removal is achieved are completely different. In a chemical-etching process, material removal is achieved by a chemical reaction at the surface, resulting in the formation of dissolved species and subsequent transportation of the dissolved species from the surface. The etching (removal) rate is constant and does not change with time. This is shown schematically in Figure 3. In the CMP process, the reactions between the chemicals and the metallic layers result in a thin, nondissolving, chemically passivating surface film that is subsequently removed by the mechanical action of the particles. Initially, the chemical reaction rate is high, but due to passivation effects, the reaction rate drops

immediately. When the surface layer is removed by the abrasive particles in the slurry, the surface-film formation and passivation phenomenon repeats itself (Figure 3). Thus, the static etch rate in CMP is quite low. In CMP of dielectric materials, although surface passivation is not a critical issue, the formation of a soft, hydrated gel-like layer on the surface is important in order to achieve high-performance polishing.

The CMP phenomena can be simulated by unbiochemical experiments that involve sliding a ball across the surface of a sample.¹³ Figure 4 shows the results obtained from abrading a tungsten substrate subjected to various chemical and electrochemical conditions with an alumina ball. The transient electrochemical current was measured during the oscillating sliding motion of the ball. The current density indicates the formation of the reacted layer on the surface. The figure shows that the layer formation rate (current density) is very high when the ball slides across the tungsten plate and decreases significantly when the ball's motion is stopped.

The CMP phenomena, especially in metals, are very similar to the results of these experiments. Slurry chemicals and particles are chosen appropriately to modulate this interaction process. The article by Singh et al. in this issue provides details on the mechanism of CMP as well as the principles behind slurry design—one of the most important and perhaps less understood aspects of the CMP process.

In mechanical polishing, the removal of material results from the direct interaction of particles on the original surface, that is, the classical abrasion-wear mechanism, which involves indentation of the surface and the removal of material by a scratching process.¹⁶ This material-removal mechanism typically requires high energy because bonds have to be broken using only mechanical forces. Due to the large energy requirements, removal rates are typically much lower than CMP unless larger-sized particles are used, in which case high surface defectivity results. Thus, an inverse relationship typically exists between the rate of removal and the fineness of the surface finish. In contrast, in a CMP process, the chemically modified surface layer is much more easily removed because of its inherent nature: a soft, ductile layer in the case of silicon and more brittle layers in the case of metals such as tungsten and copper. Figure 5 shows the relationship between removal rate and surface finish for all three material-removal processes.

Currently, the most widely used equation in CMP is Preston's law, which states that the removal rate of a material is directly proportional to the applied pressure

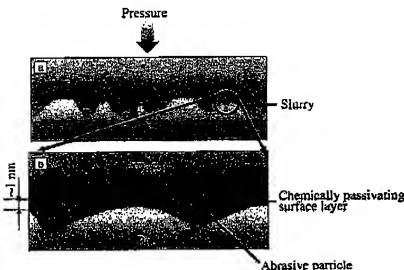


Figure 2 Schematic diagram depicting (a) microscale and (b) nanoscale phenomena that occur during CMP

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Table 1: Correlation of Systems-Level Variables with Micro- and Nanoscale Effects and Output Parameters in Chemical-Mechanical Planarization.

Input Variables	Microscale Parameters	Nanoscale Interactions	Output Parameters
Particle characteristics	Pad	Chemomechanical	Removal rate
Size	Contact area	Dynamics of surface-layer formation	Planarization
Size distribution	Pressure on the pad	Thickness	Surface finish
Shape	Particles on the pad	Uniformity	Selectivity
Mechanical properties	Pressure	Rate of formation	
Chemistry	Coverage	Layer removal mechanism	
Dispersion	Chemical concentration and distribution	Abrasion frequency	
Agglomeration			
Over-sized particles			
Slurry chemistry	Contact mode	Chemical and mechanical	
Oxidizers	Direct	Etching	
pH stabilizers	Mixed	Mechanical removal	
Complexing agents	Hydroplaning		
Dispersants			
Concentration			
pH and pH drift			
Down pressure and linear velocity			
Pad characteristics			
Mechanical properties			
Topography			
Conditioning			
Substrate characteristics			
Feature size			
Feature density			

and relative velocity of the particles across the wafer.²⁴ This equation was first suggested nearly 75 years ago for determining material removal when two plates were rubbed against each other. Subsequently, it was modified to incorporate particle-based polishing. Although this equation (with minor modifications) has been used extensively in CMP because of its apparent simplicity, it has two fundamental flaws that limit its applicability. First, this equation was developed for mechanical polishing only; without taking into account any chemical synergistic effects. Second, being a phenomenological equation, it fails to provide any insight into the interaction process, even from the mechanical viewpoint (e.g., the effects of particle size, concentration, and other slurry and pad variables). Based on these two reasons, Preston's law should not be the starting point for understanding CMP phenomena. Instead, new fundamental mechanistic approaches, which take into account synergistic mechanical and chemical effects,

and nonlinearities due to pad interactions, should be developed. The article by Singh et al. provides one such approach to address this issue.

A more elegant method for understanding the effect of the process variables is to determine the microscale and nanoscale effects that occur in CMP (Table 1). For example, if one decreases the particle size in a CMP slurry, the following micro-/nanoscale effects may occur: surface coverage of the particles on the pad may increase (microscale), material removal per particle may decrease due to lower stresses (nanoscale), and the degree of surface scratching may decrease due to reduced indentation (nanoscale). Similarly, if the chemicals are varied, the dynamics of layer formation can be altered. *In situ* measurements of these effects will represent an important step in understanding the mechanisms of the CMP process. In their article, Moirpour et al. describe some advanced analytical methods for characterizing CMP consumables and testing their interactions.

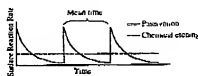


Figure 3 Schematic diagram showing the difference between CMP and chemical etching in their surface reaction kinetics. In chemical etching, the removal rate is constant and does not change with time. In the CMP process, the reactions between the chemicals and the metallic layers result in a thin, nondissolving, chemically passivating surface film, which is subsequently removed by the mechanical action of the particles. Initially, the chemical reaction rate is high, but due to passivation effects, the reaction rate drops immediately when the surface layer is removed by the abrasive particles in the slurry. The surface film formation and passivation phenomenon repeats itself.

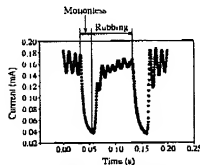


Figure 4 Transient electrochemical current measurements as a function of time for a tungsten surface abraded in an oscillating motion with an alumina pad.

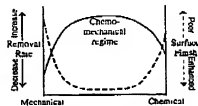


Figure 5 Schematic diagram showing the removal rate and surface finish obtained using chemical etching, mechanical polishing, and CMP.

Advances in Chemical-Mechanical Planarization

CMP Advancements and Emerging Issues

With the introduction of CMP into the mainstream semiconductor industry less than 10 years ago, several advancements in tools, the process itself, and the consumables used (particularly slurries) have taken place to meet the increasing demands of the field. Compared with single-planar tools introduced initially, the new CMP tools have several platens and employ the dry-in and dry-out concept (in which the wafer enters and exits the process in a dry state) that integrates both the polishing and the clearing processes with the same equipment.¹⁴ Nonrotating platforms that enable elliptical and linear motion have been developed.¹⁵ The tools are also equipped with state-of-the-art slurry handling systems, slurry mixing systems, and sophisticated multizone end-point detection controllers.

Significant changes have occurred in consumables, especially in the area of slurry formulation. Slurries containing smaller-sized nanoparticles and novel particles such as ceria have entered mainstream CMP applications.¹⁶ Other functional particles, such as coated and nanoporous particles, have been demonstrated for CMP.¹⁷ The development of "abrasive-free" slurries for soft materials such as copper has been an exciting new advance.¹⁷ In the abrasive-free approach, chemicals are used to soften the oxide layer on copper so that it can be removed by the mechanical action of the pad. The elimination of particles in the slurry reduces the risk of surface defectivity during the polishing process. The article by Hanazono et al. highlights this approach.

Other promising abrasive-free approaches to copper polishing have been developed.^{18,19} One such approach uses a "single-component" slurry to directly make a soft layer on the copper surface, which can then be mechanically removed by the polymer pad. An example of a blanket copper surface (copper deposited on an unpatterned water surface) before and after polishing using this method is shown in Figure 6.¹⁸ The figure shows that the as-deposited copper surface has a rms roughness exceeding 45 nm, which can be reduced to less than 2 nm after short polishing times (30–45 s). Additionally, scanning electron microscopy of the polished surface shows the scratch-free polishing capability of this approach. Abrasive-free CMP slurries have the potential to considerably simplify slurry handling and managing, reduce surface defectivity and stresses, and significantly increase polishing selectivity with respect to the underlying tantalum or dielectric layer.

Other advancements in slurry engineering include the use of additives and chemi-

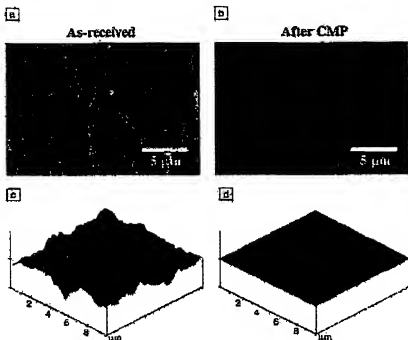


Figure 6. (a), (b) Scanning electron microscopy images and (c), (d) atomic force microscopy images of copper surfaces before (left) and after (right) the single-component abrasive-free CMP process.

cals to further control CMP performance. One example is the development of low-stress slurries for CMP of copper interconnects on low- κ substrates. The issues involved in polishing fragile low- κ materials are highlighted in the article by Bajaj et al. The mechanical fragility of low- κ dielectrics requires the use of slurries that produce low stresses on the surfaces. The softness of low- κ materials, as compared with silica, makes them susceptible to scratching, delamination, and indentation when standard abrasives are used. By manipulating the particles as well as the additives, shear stress from the slurries can be significantly reduced. Figure 7 shows friction force measurements during polishing of a copper/low- κ dielectric (carbon-doped silica) surface using standard silica abrasives and formulated slurries with specific additives.¹⁹ The figure shows that shear forces can be significantly decreased by the use of specific additives in the slurry. One expects this type of approach to be further emphasized with the introduction of low- κ materials in semiconductor production in the coming decade.

Another important area that is expected to show significant advancement is high-

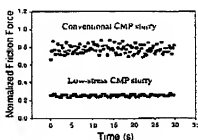


Figure 7. Friction force measurements for conventional and low-stress CMP slurries used to polish a copper/low- κ dielectric surface.

planarity polishing of dielectric materials. Due to widely varying topographies of the surface, slurries have to be designed that will enhance the planarity of the polishing process. The polish rate of typical particle-based slurries increases linearly with applied pressure. Although this leads to planarization of the surface, slurries that have an even higher planarization capability are required, due to varying

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pattern densities and periodicities. One method developed for 3M is the use of a pad embedded with abrasive silica/ceriated particles.²⁰ These pads have been used to achieve high-planarity polishing of silica for shallow trench isolation (STI) applications. Studies that exhibit non-Freeman variations in polish rate as a function of pressure, resulting in high-planarity polishing, are expected to be used in the future for both dielectric and metal applications.⁹

The rapid miniaturization of semiconductor devices has placed more exacting requirements on the CMP process. Smaller devices require a high degree of control, and the manufacturing operation has a smaller process window. An example of these more stringent requirements is the STI process, which is used to isolate adjacent devices on a wafer. Issues such as nanotopography (nanometric changes across a millimeter length scale) may significantly lead to nonplanarity and limit our ability to achieve high-yield CMP processes. The article by Boring and Lee focuses on the effect of nanotopography in STI pushing.

Emerging Applications

With the increased popularity of planarization with CMP technology to planarize surfaces and fabricate embedded submicron structures through polishing, new applications of this technology are expected to emerge at a rapid rate. The growth of microchip complexity based only on silicon technology is fast approaching fundamental limits.²¹ New technologies that incorporate novel materials and structures onto silicon may become the driving force to successfully maintain or accelerate Moore's law (Gordon Moore's prediction that the computing power of a chip will double every 12–18 months). CMP is expected to play a key role in these next-generation micro- and nanofabrication technologies. Some of the potential areas in which CMP could play a significant role include the formation of gate electrodes for high- κ dielectrics, gate structures and interconnect technology for ferroelectric and ferroelectric nonvolatile memories, STI applications in high-speed Si-Ce devices, planarization of multidimensional microelectromechanical systems (MEMS), fabrication of three-dimensional membranes and optical-bandgap materials, and planarization of III-V semiconductor structures (aluminum nitride, gallium nitride, silicon carbide, diamond, etc.) for high-quality epitaxial growth. The article by Evans focuses on some future applications of CMP.

In all of these applications, CMP is considered an enabling technology, and its ap-

plications are expected to expand to more chemically complex materials and mechanically fragile structures. In this regard, there is immense room for integration of new fabrication technologies on silicon. An example of this is shown in the integration of embedded metal and oxide structures onto silicon by means of CMP.¹⁹ Figure 8a shows a cathodoluminescent image of europium-doped yttrium oxide phosphor structures embedded in silica using CMP. These structures exhibit much brighter cathodoluminescence than a blanket flat film, thus showing great potential for field-emission display applications. Another example of the integration of novel material structures onto silica is shown in Figure 8b. This figure shows embedded magnetic submicron cobalt structures distributed periodically inside a silica matrix. To make this structure, a conformal film of tantalum is deposited inside silica vias, followed by electrochemical deposition of cobalt and then planarization. Such structures are expected to be utilized in 3D patterned storage media or other device

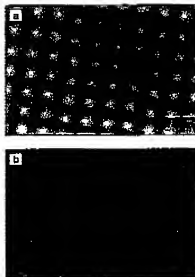


Figure 8. Example of novel embedded structures obtained by CMP.

(a) Europium-doped yttrium oxide phosphor structures embedded in silica using CMP. These structures exhibit much brighter cathodoluminescence than a blanket flat film, thus showing great potential for field-emission display applications. (b) Magnetic submicron cobalt structures embedded in a silica matrix. Such structures are expected to be used in three-dimensional patterned storage media or other device structures.

structures. It is expected that with further advancements in photolithography, even smaller nanoscale embedded structures will be fabricated in the future.

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